THE ACTION OF ACID HALIDES ON ALDEHYDES AND KETONES

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Ernest Henry Vollweiler

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E H Vollweiler.

INTRODUCTION.

Although the addition and condensation reactions of aldehydes and ketones were among the first studied reactions in organic chemistry, and although they have been for the most part carefully investigated, it is a surprising fact that their action with acid halides has received comparatively little attention. This may be partly due to the fact that many of the compounds obtained by such condensations are very unstable solids, while others are liquids which cannot be distilled even under diminished pressure without the splitting out of halogen acid.

Since 1857 several investigators have prepared a number of addition compounds of aliphatic aldehydes and ketones with acid chlorides and bromides, and incidentally their structure was proved.

In the aromatic series, however, only one or two examples of such addition compounds have been reported. Thus it was shown that chlorine acting on benzaldehyde yields an unstable liquid which corresponds in empirical formula to the addition product of benzoyl chloride and benzaldehyde, but this was not further investigated. Claisen[1] reported that benzoyl bromide and benzaldehyde give a solid compound, but beyond a superficial examination, gave it no more attention. Other examples of possible condensations of this kind in the aromatic series were not found.

The present investigation was made, first, to find out empirically whether the condensation of aliphatic and aromatic halides with aromatic aldehydes is a general one, and second, to study the ease of formation, the reactions, and the structure of the compounds produced.

HISTORICAL.

By the action of chlorine on acetaldehyde in a closed tube, Wurtz[2] obtained a compound the empirical formula of which was $C_4 H_7 O_2 Cl$. He believed that this was formed by a preliminary change of the aldehyde into its polymer $C_8H_8O_2$, and that one hydrogen atom of this was then substituted by a chlorine atom. Later, Simpson[3] found that the same compound is formed by the reaction of acetyl chloride on acetaldehyde, when they are heated together in a closed tube. He concluded that the formation of the compound by the action of chlorine on acetaldehyde is due to the preliminary formation of acetyl chloride,and this subsequently combines with a molecule of acetaldehyde to give the addition compound. Franchimont[4] prepared the same compound in a somewhat purer state using paraldehyde in place of the acetaldehyde. Finally, Schiff[5] showed the structure of the addition compound to be $CH_3CHCl\text{-}O\text{-}CO\text{-}CH_3$; for by treating it with potassium acetate, he obtained ethylidene diacetate, which had been previously prepared by Geuther[6] by the action of acetic anhydride on acetaldehyde.

Rubencamp[7] treated a number of aliphatic halides with acetaldehyde, and by the action of silver salts of fatty acids on these compounds, he obtained ethylidene derivatives homologous with the ethylidene diacetate obtained by Schiff. The following table represents the results of Rubencamp's work:-

Addition product	B.P.	Treated with	Product	B.P.
Acetaldehyde Acetyl chloride	121.5°	Silver acetate	Ethylidene-diacetate	168.8°
Acetaldehyde Propionyl chloride	135°	Silver propionate	Ethylidene-dipropionate	192.2°
Acetaldehyde Buteryl chloride	149°	Silver butyrate	Ethylidene-dibutyrate	215.5°
Acetaldehyde Valerianyl chloride	162°	Silver valerianate	Ethylidene divalerianate	225°
Acetaldehyde Acetyl chloride	121.5°	Silver propionate	Ethylidene-acet-propionate	176.8°
Acetaldehyde Propionyl chloride	135°	Silver acetate	Ethylidene-acet-propionate	176.8°
Acetaldehyde Acetyl chloride	121.5°	Silver butyrate	Ethylidene-acetbutyrate	192.8°
Acetaldehyde Acetyl chloride	121.5°	Silver valerianate	Ethylidene-acet-valerianate	194.9°

Other examples of the action of certain aliphatic aldehydes and ketones on acid chlorides and bromides have appeared in the literature. Henry[8] showed that formaldehyde or its polymer, polyoxymethylene, reacts with acetyl chloride in the same way as acetaldehyde:

$$CH_3COCl + HCHO \longrightarrow HCHCl\text{-}O\text{-}CO\text{-}CH_3$$

Franchimont[4] mentions that Tawildaroff obtained an unstable addition product from acetyl bromide and acetaldehyde.

Lees[9] worked with higher aliphatic aldehydes and ketones. The study of these compounds was complicated by the fact that halogen acid was split off from the resulting product. When ketones are used, the halogen acid may split off in two ways, so that Lees was

unable to determine which isomer he obtained. He found that when molecular amounts of methyl-n-nonyl ketone and benzoyl chloride are refluxed for several hours, the benzoyl chloride adds to the carbonyl group of the ketone, followed by a subsequent splitting out of hydrogen chloride;

$$CH_3CO\text{-}C_9H_{19} + C_6H_5COCl \longrightarrow C_9H_{19}\text{-}\underset{\underset{CH_2}{\|}}{C}\text{-}O\text{-}CO\text{-}C_6H_5$$

$$\text{or } C_8H_{17}CH = \underset{\underset{CH_3}{|}}{C}\text{-}O\text{-}CO\text{-}C_6H_5$$

No action resulted when acetone or methyl-n-propyl ketone were refluxed with benzoyl chloride. He believed this was due to the fact that in each case one of the compounds used has a boiling point lower than the temperature at which the reaction will take place. In support of this, he showed that by refluxing methyl-n-nonyl ketone with valerianyl chloride, he obtained a reaction just as in the case of benzoyl chloride with the same ketone. He also obtained analogous products from benzoyl chloride and each of the following: methyl-n-butyl ketone, methyl-sec.hexyl ketone, methyl-n-heptyl ketone, acetophenone, camphor, and heptaldehyde. In the last three cases, hydrogen chloride could split out in only one way, hence no isomeric structure is possible. In no case however did he obtain simple addition compounds.

Descude[10] in his study of anhydrous zinc chloride as a catalyzer, found that it greatly increases the speed with which certain aldehydes and ketones will unite with acid chlorides. In some cases it will cause reactions to take place which show no tendency at all to do so in the absence of the zinc chloride. As has al-

ready been mentioned, Simpson[3] found that it is necessary to heat acetyl chloride and acetaldehyde together in a sealed tube in order to get them to react; but in the presence of a trace of zinc chloride, Descude found that the reaction went easily in the cold. Louis Henry[8] obtained an addition between formaldehyde and acetyl chloride by heating them together in a sealed tube; in this case also, a trace of zinc chloride causes the reaction to give the addition compound to go in the cold.

In the aromatic series, Descude found that the reactions go in the same way, but the influence of the zinc chloride is even more marked. Benzoyl chloride in the presence of zinc chloride was found to give an addition compound with formaldehyde, and benzaldehyde reacted very energetically with either acetyl or benzoyl chloride under similar conditions; but Descude could not isolate any definite compounds.

Descude found that aliphatic ketones do not form stable addition compounds with acetyl or benzoyl chlorides, even in the presence of zinc chloride. Thus acetone, in the presence of acetyl chloride and zinc chloride, gave mesityl oxide by the condensation of two molecules of acetone, and phorone by the condensation of three molecules. Benzoyl chloride in place of acetyl chloride gave the same products. Descude showed that the reaction will not go in the absence of the acid chloride, the function of which he explained as follows:

(1) $$(CH_3)_2CO + CH_3\text{-}CO\text{-}CH_3 + CH_3CO\text{-}Cl \longrightarrow CH_3COOH + (CH_3)_2CCl\text{-}CH_2\text{-}CO\text{-}CH_3$$

(2) $$(CH_3)_2CCl\text{-}CH_2\text{-}CO\text{-}CH_3 \longrightarrow (CH_3)_2C = CH\text{-}CO\text{-}CH_3 + HCl$$

Zinc dust has also been found to catalyze the action of acid chlorides on aldehydes and ketones. Paal[11] found that benzaldehyde and acetyl chloride in the presence of zinc dust react vigorously, giving hydrobenzoin-diacetate, whose formation he explains as follows:

$$\begin{matrix} C_6H_5\text{-}CHO \\ C_6H_5\text{-}CHO \end{matrix} + \begin{matrix} CH_3\text{-}CO\text{-}Cl \\ CH_3\text{-}CO\text{-}Cl \end{matrix} + Zn \longrightarrow ZnCl_2 + \begin{matrix} C_6H_5\text{-}CH\text{-}O\text{-}CO\text{-}CH_3 \\ | \\ C_6H_5\text{-}CH\text{-}O\text{-}CO\text{-}CH_3 \end{matrix}$$

He noted that aliphatic acid chlorides and aliphatic aldehydes react in the same way. Acetyl chloride also reacts with benzophenone in a similar manner, the product being α-benzpinakoline or, if an excess of acetyl chloride is used, β-benzpinakoline. The mechanism of their formation, by analogy to the mechanism given for benzaldehyde, is as follows:

$$\begin{matrix} (C_6H_5)_2{=}C{=}O \\ (C_6H_5)_2{=}C{=}O \end{matrix} + \begin{matrix} CH_3\text{-}CO\text{-}Cl \\ CH_3\text{-}CO\text{-}Cl \end{matrix} + Zn \longrightarrow ZnCl_2 + \begin{matrix} (C_6H_5)_2{=}C\text{-}O\text{-}CO\text{-}CH_3 \\ | \\ (C_6H_5)_2{=}C\text{-}O\text{-}CO\text{-}CH_3 \end{matrix}$$

$$\longrightarrow \quad \begin{matrix} (C_6H_5)_2{=}C \\ | \\ (C_6H_5)_2{=}C \end{matrix}\!\!>\!O \quad + \quad (CH_3\text{-}CO)_2{=}O.$$

Paal did not, however, isolate any intermediate addition compounds.

As early as 1832, Wöhler and Liebig[12] in attempting to prepare benzoyl bromide by the action of bromine on benzaldehyde, obtained a semi-solid material which they thought to be benzoyl bromide. This received no further attention until Claisen[1] in making pure benzoyl bromide, found that when the benzoyl bromide is mixed with an equivalent amount of benzaldehyde, it gives the same substance which Wöhler and Liebig had obtained by the action of bromine on benzaldehyde. Claisen purified the compound by re-

crystallization from petrol ether, and from a bromine determination showed the empirical formula was $C_{14}H_{11}BrO_2$. The compound was rather unstable in the air, but beyond this he did not investigate either its properties or structure, which he suggested was perhaps C_6H_5-CHBr-O-CO-C_6H_5. No later work on such bromine compounds can be found.

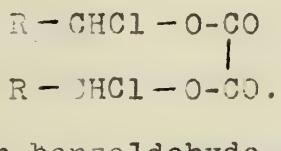
Staudinger and Anthes[13] obtained a colorless crystalline solid by the reaction of benzoyl iodide and benzaldehyde in petrol ether solution. The compound, which they assumed to be iodbenzylbenzoate, melted at about 60°, but was very unstable.

Claisen[1] stated that benzoyl bromide will easily give a solid compound with acetone, but later Franchimont[4] repeated the work and found that the solid substance obtained was nothing but benzoic acid.

Chlorine has been found to react with benzaldehyde in the same way as bromine; Laurent and Gerhardt[14] obtained in this way a compound whose empirical formula was $C_{14}H_{11}ClO_2$. Schiff[15] obtained the same liquid by the action of benzoyl chloride on benzaldehyde.

The reactions of oxalyl chloride with aromatic aldehydes and ketones to give compounds with the oxygen replaced by two chlorine atoms were investigated by Staudinger[13]. The types of aldehydes and ketones which were tried are represented by the following compounds:- benzaldehyde, benzophenone, dimethylamino-benzaldehyde, and dimethyl-amino-benzophenone. In every case, the application of more or less heat caused the oxalyl chloride to convert the carbonyl group of the aldehyde or ketone into the keto chloride group $C{=}Cl_2$. In two cases, however, benzaldehyde and

cinnamyl aldehyde addition products were isolated, presumably as intermediate compounds. When benzaldehyde (I mole) was allowed to stand several days with oxalyl chloride (2 moles) in petrol ether solution, a solid crystallized out. This solid was quite unstable, and decomposed before melting point could be reached. Cinnamyl aldehyde unites with oxalyl chloride in the same ratio to give a somewhat more stable compound, whose structure Staudinger believed to be



In the case of both benzaldehyde and cinnamyl aldehyde, a high temperature causes the carbonyl group to be converted into the keto chloride group.

Staudinger[13] found that benzaldehyde reacts with oxalyl bromide much more rapidly than with oxalyl chloride; the addition product of two moles of the aldehyde with one of oxalyl bromide was a solid which melted at 131°. The compound was unstable and quickly decomposed in the air.

THEORETICAL.

I. Formation of Addition Compounds.

Addition compounds of acid halides with aldehydes are formed in both the aliphatic and aromatic series, but a marked difference exists between the conditions under which aliphatic acid halides will unite with aliphatic aldehydes, and the conditions under which the reactions of aromatic acid halides with aromatic aldehydes will take place. The investigators who studied the former addition reactions found that it was necessary to heat the mixture of the aliphatic acid halide and the aldehyde, in some cases in bombs, to cause the reaction to take place. In most cases in the aromatic series, on the other hand, the reactions go of their own accord at room temperature, and in many cases with the evolution of considerable heat. The same is true of the cases where oxalyl bromide was used in place of an aromatic acid halide.

In the aromatic series, the compounds differ greatly among themselves in the ease of formation of the addition compounds; thus, benzoyl bromide gradually reacts with benzaldehyde so that the addition compound crystallizes out in a day or two; with other aldehydes, of which methyl vanillin is an example, benzoyl bromide reacts vigorously with the evolution of heat, and crystals of the addition compound are obtained in a few hours; and finally benzaldehyde reacts exceedingly slowly with acid halides of the type of para-nitrobenzoyl chloride, which required three months before the material crystallized. Acetvanillin reacts more slowly than methyl vanillin with benzoyl bromide, and no heat effect is apparent; and vanillin reacts more rapidly than either of these two substitution products of vanillin. Anisaldehyde reacts more

rapidly with benzoyl bromide than nitroanisaldehyde does, and piperonal more rapidly than brompiperonal. Benzoyl chloride has been found to react more slowly with benzaldehyde than benzoyl bromide does, and benzoyl iodide[13] more rapidly than either the chloride or bromide. Similarly, para-nitrobenzoyl chloride reacts much more slowly than the corresponding para-nitrobenzoyl bromide. Aromatic acid chlorides with chlorine or bromine in the ring apparently did not react at all with benzaldehyde, even after standing for several weeks.

The above examples seem to indicate that negatively substituted rings of either the aldehyde or of the acid halide cause the addition compounds to form more slowly and to be more stable. Other addition products show however that no general conclusions can be drawn as to the rate of formation of the crystalline addition compounds. For example, benzaldehyde and benzoyl bromide require a day or two before crystals begin to form, while the negatively substituted ortho- and para-brombenzaldehydes form crystalline addition compounds with benzoyl bromide in the course of a few hours; and paranitrobenzaldehyde with benzoyl bromide gives a crystalline addition product after standing a day.

It is also interesting to compare the effect of substituting groups in the ring of the acid halide with the effect of the same group in the ring of the aldehyde. The two examples chosen for this were paranitrobenzaldehyde with benzoyl bromide, and benzaldehyde with paranitrobenzoyl bromide. The former addition compound was formed more slowly and was somewhat more stable than the latter.

From the instances already mentioned and an examination of the list of addition compounds given at the end of this section, it is evident that the substituting groups in the ring of either the aldehyde or of the acid halide have a marked influence on the speed of formation of the addition compounds. In the majority of cases, the presence of negative substituents in either ring cause the formation of the addition products to go more slowly; but no general conclusion can be drawn from these cases, for in several instances negatively substituted rings have been found to form crystalline addition compounds more rapidly than unsubstituted rings do. In all cases, however, negative substituents in either ring caused the addition reactions to go more smoothly, and the addition compound to be more stable, than in the cases of unsubstituted or positively substituted rings. For example, the addition compound of benzaldehyde and benzoyl bromide is unstable in the air, and decomposes entirely into benzaldehyde and benzoic acid in the course of a few hours; the addition product of methyl vanillin and benzoyl bromide decomposes in less than ten seconds when exposed to the air; the addition compound of acetvanillin and benzoyl bromide shows little change after standing several hours in the air; and finally, the addition product of paranitrobenzoyl chloride and benzaldehyde is stable in the air for an indefinite length of time. The stability in water follows the same order; cold water rather rapidly decomposes the first two addition compounds mentioned above; but the latter can remain in cold water for days without decomposition, and even cold sodium carbonate solution does not affect it appreciably in several hours time. It is somewhat remarkable that in many cases the decomposition seems

to proceed almost as rapidly in the air as in cold water; the addition product of benzaldehyde and benzoyl bromide requires five or ten minutes boiling with water to decompose it completely. Aromatic acid iodides give addition compounds which are less stable than those of acid bromides, and these in turn are less stable than those of acid chlorides; the stability usually varies inversely with the ease and speed of formation.

Oxalyl bromide reacts very readily with aromatic aldehydes, and resembles the aromatic rather than the aliphatic acid halides in these reactions. It differs from the aromatic acid halides, however, in that the reactions with aldehydes usually go smoothly in ether solution, and the addition compounds can more frequently be obtained and isolated in the pure state.

A summary of the addition compounds which have been prepared together with some of the properties of the products formed, is given in the following table:-

Acid Halide	Aldehyde	Time of Reaction	Ratio	m.p.	Stability in air.
Oxalyl bromide	Benzaldehyde	5 min.	1:2	131°	Decomposed in several hours
" "	Cinnamic Aldehyde	2 hrs.	1:2	85-86°	Decomposed in several hours
" "	Anisaldehyde	½ hr.	1:2	About 66°	Decomposed in ½ hour
" "	Nitroanisaldehyde	4 days	1:2	116-118°	No decomposition in 1 day
" "	o-nitrobenzaldehyde	1 hr.	1:2	158-162°	No decomposition several days.
" "	m- " "	2 days	1:2	128-129°	Slightly decomposed in one day.
" "	p- " "	.....	...	.....	No reaction in 6 months.
" "	Piperonal	5 min.	1:2	81-83°	Decomposed in ½ hour.
" "	Furfural	5 min.	1:2	76½-77°	Decomposed in ½ hour
" "	Salicylaldehyde	2 min.	...	....	Unstable red liquid.
" "	Methyl salicylaldehyde	5 min.	1:2	99°	Decomposed in several hours
" "	Vanillin	2 min.	1:2	93-95°	Decomposed in 1 hour.
" "	Acetvanillin	2 hours	1:2	142-143°	Slightly decomposed in 2 hours.
" "	o-brombenzaldehyde	10 "	1:2	140°	No decomposition in 5 days
" "	p-dimethylaminobenzaldehyde	2 min.	...	102-103°	Slight decomposition in ½ hour.
Benzoyl bromide	Benzaldehyde	2 days	1:1	67°	Decomposed in 1 day.
"					

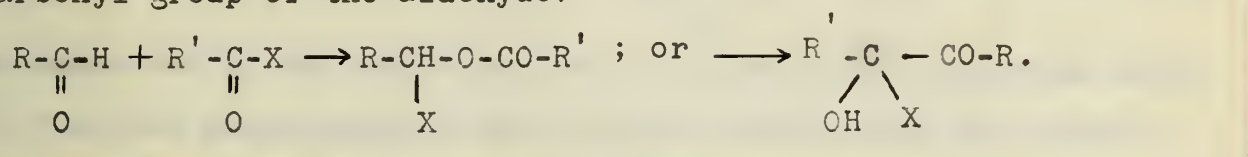
Acid Halide	Aldehyde	Time of Reaction	Ratio	m.p.	Stability in air
Benzoyl bromide	p-nitrobenzaldehyde	1 day	1:1	89-90°	No decomposition in several days.
" "	o-brombenzaldehyde	7 hours	1:1	106-107°	Slightly decomposed in 5 days
" "	p-brombenzaldehyde	3 hours	1:1	110°	Slightly decomposed in 10 hours.
" "	Anisaldehyde	Vigorous reaction, product did not crystallize.			
" "	Nitroanisaldehyde	3 hours	1:1	101-102°	Slightly decomposed in 1 hour.
" "	Salicylaldehyde	Vigorous reaction, product did not crystallize.			
" "	Methyl salicyl-aldehyde	1 hour		About 50°	Decomposed in less than 10 seconds.
" "	Vanillin	Vigorous reaction, product did not crystallize.			
" "	Methyl vanillin	½ hour		About 100°	Decomposed in 10 seconds
" "	Acetvanillin	2 hours	1:1	102-103°	Decomposed in several days
" "	Terephthalic aldehyde	3 hours	1:1	153-162°	Decomposed in several days
" "	Piperonal	2 days		About 105-110°	Decomposed in a few sec.
" "	Brom-piperonal	½ hour	1:1	108-113°	Decomposed in several days

Acid Halide	Aldehyde	Time of Reaction	Ratio	m.p.	Stability in air.
Benzoyl bromide	Furfural	Vigorous reaction, giving a charred mass.			
" "	Heptaldehyde	Vigorous reaction, giving a mixture of products			
" "	Chloral	No reaction in 6 months.			
Oxalyl chloride	Vanillin	Vigorous reaction, no isolatable product.			
Acetyl chloride	Benzaldehyde	Reaction gives a liquid which could not be purified.			
Benzoyl chloride	Brom-methyl vanillin	7 days	1:1	158-160°	Decomposed in several days.
" "	Brom-piperonal	7 days	1:1	97-102°	Slightly decomposed in 2 days.
o-nitrobenzoyl chloride	Benzaldehyde	1 week	1:1	81-82°	Not decomposed in several months
m-nitrobenzoyl chloride	"	3 months	1:1	87-88°	Not decomposed in several months
p-nitrobenzoyl chloride	"	5 days	1:1	118-118½°	Not decomposed in several months
p-nitrobenzoyl bromide	"	15 min.	1:1	132°	Slight decomposition in several days.
Toluene-sulfonyl chloride	"	No reaction			

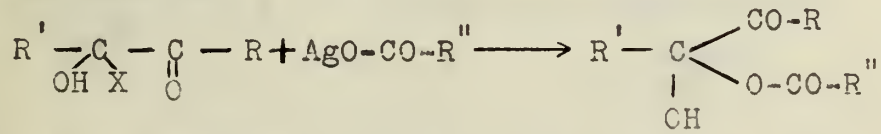
Acid Halide	Aldehyde	Time of Reaction	Ratio	m.p.	Stability in air.
p-chlorbenzoyl chloride	Benzaldehyde	No reaction.			
p-brombenzoyl chloride	"	No reaction			
o-brombenzoyl chloride	"	No reaction.			

2. Structure of the Addition Compounds.

Since an acid halide and an aldehyde each contain a carbonyl group, it is possible that the aldehyde may add to the carbonyl group of the acid halide or that the acid halide might add to the carbonyl group of the aldehyde:



If the second formula is correct, we should expect the addition compounds to be very unstable, and to split out halogen acid very quickly; for the compound has a hydroxyl and halogen on the same carbon atom and such a structure is in general very unstable. It was found that many of the addition compounds do split out halogen acid easily in the air but this actionwas not observed when air was excluded; many other compounds showed no tendency at all to split out halogen acid in the air so that it must be concluded that in the cases where halogen acid does split out, it is due to the moisture of the air. Moreover, if the second structure is correct, silver salts of organic acids should react with it in the following manner:



but instead of compounds of this type being obtained, the reaction yields compounds of the type of benzylidene dibenzoate, $C_6H_5 - CH{=}(O\text{-}CO\text{-}C_6H_5)_2$. The results of other reactions with various reagents, aniline for example, are also difficult to explain on the basis of such a structure of the addition product.

Moreover, the carbonyl group of an acid halide does not show nearly so great a tendency of addition as the carbonyl group of an aldehyde does. The second suggested structure is therefore highly improbable.

The first structure, namely $R-\underset{\underset{X}{|}}{CH}-O-CO-R'$, on the other hand is supported by the reactions which the addition compounds undergo. Various investigators have already proved that the corresponding addition compounds in the aliphatic series have this structure, hence a similar structure is to be expected in the aromatic series. In the cases where oxalyl bromide is the acid halide used, two molecules of the aldehyde should be expected to unite with one molecule of oxalyl bromide:

$$2R-\underset{\underset{O}{\|}}{C}-H + Br-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-Br \longrightarrow R-\underset{\underset{Br}{|}}{CH}-O-CO-CO-O-\underset{\underset{Br}{|}}{CH}-R$$

The structure of these compounds was investigated by means of the action of silver salts of organic acids on the addition compounds. Silver salts should react with the above structures as follows:

$$R-\underset{\underset{Br}{|}}{CH}-O-CO-R' + R''-CO-OAg \longrightarrow R-\underset{\underset{O-CO-R''}{|}}{CH}-O-CO-R'$$

Thus, silver benzoate acting on the addition product of benzaldehyde and benzoyl bromide should give benzylidene dibenzoate if the suggested structure is correct:

$$C_6H_5-\underset{\underset{Br}{|}}{CH}-O-CO-C_6H_5 + AgO-CO-C_6H_5 \longrightarrow C_6H_5-CH=(O-CO-C_6H_5)_2 + AgBr$$

Now benzylidene dibenzoate has been synthesized by Wegscheider and Späth[16] by the reaction of benzaldehyde with benzoic anhydride in the presence of a small amount of concentrated sulfuric acid:

$$C_6H_5-\underset{\underset{O}{\|}}{C}-H+(C_6H_5-CO)_2=O \xrightarrow{H_2SO_4} C_6H_5-CH=(O-CO-C_6H_5)_2.$$

The compound obtained by the reaction of silver benzoate with the addition product proved to be identical with the compound obtained by Wegscheider and Späth. The addition compound is therefore brombenzylbenzoate, and the suggested structure of the addition compounds is correct.

Similar reactions which led to the same conclusions as to the structure, were those of silver acetate on the addition product of benzaldehyde and benzoyl bromide, and silver benzoate on the addition product of benzaldehyde and paranitrobenzoyl chloride. These yielded respectively, benzylidene benzoate-acetate and benzylidene benzoate-paranitrobenzoate.

Attempts to synthesize brombenzylbenzoate by the reaction $C_6H_5-CH_2-O-CO-C_6H_5+Br_2 \longrightarrow C_6H_5-CHBr-O-CO-C_6H_5+HBr$, and the addition product of oxalyl bromide and benzaldehyde as follows: $(C_6H_5-CH_2-O-CO)_2+2\ Br_2 \longrightarrow (C_6H_5-CHBr-O-CO)_2+2\ HBr$, were unsuccessful. Some benzyl bromide was obtained in each case showing that the bromine breaks up the molecule.

3. Reactions of the Addition Compounds.

The reactions of the addition compounds are in some cases normal replacement reactions, while in other cases the addition

compounds react as though they were simple mixtures of the substances from which they are produced. Thus ammonia was found to react with brombenzylbenzoate to give benzamide and benzaldehyde:

$$C_6H_5\text{-}CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + 2NH_3 \longrightarrow C_6H_5\text{-}CO\text{-}NH_2 + C_6H_5\text{-}CHO + NH_4Br,$$

and Staudinger[13] has found that when aniline acts on the addition product of oxalyl bromide and benzaldehyde in ether solution oxanilide is formed:

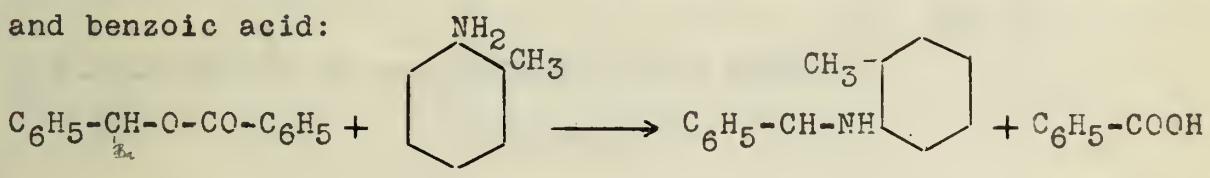
$$(C_6H_5\text{-}CHBr\text{-}O\text{-}CO\text{-})_2 + 4\ C_6H_5\text{-}NH_2 \longrightarrow (CO\text{-}NH\text{-}C_6H_5)_2 + 2\ C_6H_5\text{-}CHO$$

$$+\ 2\ C_6H_5\text{-}NH_2.HBr\ .$$

Brombenzylbenzoate and aniline on the other hand, were found not to give benzanilide as might be expected from the above reactions, but benzylidene aniline and benzoic acid instead:

$$C_6H_5\text{-}\underset{\underset{Br}{|}}{CH}\text{-}O\text{-}CO\text{-}C_6H_5 + C_6H_5\text{-}NH_2 \longrightarrow C_6H_5\underset{\underset{Br}{|}}{CH}\text{-}\underset{\underset{H}{|}}{N}\text{-}C_6H_5 + C_6H_5\text{-}COOH$$

and similarly, ortho-toluidine gave benzylidene ortho-toluidine and benzoic acid:



The above reactions with aniline or substituted anilines do not take place in ether solution at 0°, but when the solution is allowed to come to room temperature the reaction quickly takes place. Not a trace of benzanilide was formed by the action of aniline on the addition compound. This proves that the addition compound remains intact even though the reaction with aniline goes very vigorously when no solvent is used for if the heat of the reaction should partly break up the addition compound into benzaldehyde and benzoyl bromide, the latter would undoubtedly immediately give

benzanilide. The mechanism of the reaction with aniline is therefore probably

$$C_6H_5\text{-}CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + HN(H)\text{-}C_6H_5 \longrightarrow C_6H_5\text{-}\underset{\underset{Br}{|}}{CH}\text{-}\underset{\underset{H}{|}}{N}\text{-}C_6H_5 + C_6H_5\text{-}COOH$$

and on subsequent treatment with alkali:

$$C_6H_5\text{-}\underset{\underset{Br}{|}}{CH}\text{-}\underset{\underset{H}{|}}{N}\text{-}C_6H_5 + NaOH \longrightarrow C_6H_5\text{-}CH{=}N\text{-}C_6H_5 + NaBr + H_2O$$

The main products of the reaction of ethyl alcohol and brombenzylbenzoate were found to be ethyl benzoate and benzaldehyde; the course of the reaction is probably as follows:

$$C_6H_5\text{-}CHBr\text{-}O\text{-}CO\text{-}C_6H_5 + C_2H_5OH \longrightarrow C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}H + C_6H_5\text{-}COOC_2H_5 + HBr$$

Metals such as zinc and copper, would be expected to react with the addition products as follows:

$$2\ R\text{-}\underset{\underset{Br}{|}}{CH}\text{-}O\text{-}CO\text{-}R' + Zn \longrightarrow R\text{-}\underset{\underset{R\text{-}CH\text{-}O\text{-}CO\text{-}R}{|}}{CH}\text{-}O\text{-}CO\text{-}R + ZnBr_2$$

Brombenzylbenzoate was found to react vigorously with zinc and more slowly with copper but the reaction products consisted of benzaldehyde and viscous liquids which were not identified. Sodium malonic esters (methyl and ethyl) also reacted with brombenzylbenzoate to give benzaldehyde and other liquids which were not identified.

4. Summary.

The formation of addition compounds of aromatic acid halides and of oxalyl bromide with aromatic aldehydes has been found to be a fairly general reaction; the only exceptions found are halogen substituted acid chlorides and toluene sulphonyl chlorides which apparently undergo no reactions with aromatic aldehydes at room temperature. These compounds also would perhaps give crystalline addition compounds if a higher temperature or a suitable catalyst were used.

The mechanism of formation of the addition compounds has been investigated and their structure has been proved.

From a study of the various addition products which have been mentioned, it is evident that the formation of addition compounds between acid halides and aromatic aldehydes depends upon the nature of the substituent groups present in the reacting molecules. An appreciable difference exists between the addition products in which the substituting group is present in the aldehyde nucleus and those in which it is present in the acid halide nucleus. Positive groups such as methyl or methoxy in the aldehyde nucleus cause the addition reactions with benzoyl bromide to proceed so rapidly that the molecule is in some cases broken down by the reaction. Benzaldehyde reacts more smoothly and in most cases more slowly than the positively substituted aldehydes, while negatively substituted aldehydes or acid halides give still more smooth reactions. Although no general rule can be laid down with respect to the comparative speeds with which the variously substituted rings will react, in most cases negatively substituted rings react more slowly than unsubstituted or positively substituted rings.

Acid chlorides react much more slowly than the bromides and these in turn more slowly than the iodides.

Oxalyl bromide forms crystalline addition compounds with aromatic aldehydes in the ratio of two molecules of the aldehyde to one of the acid bromide. The addition compounds of oxalyl bromide are formed more readily and are somewhat more stable than the corresponding compounds of benzoyl bromide.

The rate of formation, stability and reactions of the addition compounds have been investigated.

5. Substitution Reactions of Oxalyl Bromide.

Oxalyl bromide reacts with the carbonyl group of some aldehydes and ketones to give the keto-bromide group $>C=Br_2$. When aldehydes were treated with oxalyl bromide an addition product was first formed in every case. A higher temperature was required to break up the addition compound to bive the keto-bromide and in some cases decomposition of the addition product set in before the temperature was reached at which the keto-bromide was formed. With benzaldehyde, oxalyl bromide gives benzal bromide, which has previously been prepared in various ways and for which the boiling points given by various investigators vary widely. Vorländer[17] prepared benzal bromide by the action of hydrogen bromide on benzaldehyde and found its boiling point to be 119-124° under 20-25 mm The product obtained by the action of oxalyl bromide on benzaldehyde boiled at 120-24° under 20 mm. The boiling points of the products obtained by other investigators vary widely from the

boiling points given above and their compounds were evidently impure. The yield of benzal bromide is much better when made by the use of oxalyl bromide than when hydrobromic acid is used according to the method of Vorländer. From 30 grams pure benzaldehyde, Vorländer obtained 18 grams pure benzal bromide, whereas the oxalyl bromide method yields a weight of benzal bromide equal to that of the benzaldehyde used. Furthermore, to get the above yield by the hydrobromic acid method, Vorländer allowed the mixture to stand three weeks, whereas by the oxalyl bromide method the reaction is complete in a few hours.

The use of oxalyl bromide to replace the oxygen atom of aldehyde by bromine is of limited application however, because often the addition compound, which is first formed in all cases,decomposes when heated and no replacement of the oxygen occurs. An example of this is found in the case of cinnamyl aldehyde which will not yield cinnamyl-dibrom-methane. Oxalyl bromide works much better with ketones both in the aliphatic and aromatic series. The yields are usually good and the process is quite simple. In the aliphatic series of course the replacement of the oxygen by bromine may be followed by a splitting out of hydrobromic acid and this was found to be the case in every instance tried.

Adams and Wirth[18] found that oxalyl chloride reacts with chromic anhydride to give a good yield of chromyl chloride. A similar reaction to give the unknown chromyl bromide by the use of oxalyl bromide suggested itself but the attempt to prepare it in this way was unsuccessful although the reaction was carried out under various conditions.

EXPERIMENTAL.

I. ADDITION REACTIONS OF BENZOYL BROMIDE.

Benzoyl Bromide and Ortho-brombenzaldehyde.

No reaction was apparent when 3.5 grams (1 mole) benzoyl bromide was added to 3.5 grams (1 mole) ortho-brombenzaldehyde, but after standing seven hours the material crystallized. The crystals were washed with a little dry ether and recrystallized from hot ligroin. A practically theoretical yield of perfectly white crystals, m.p. 106-107°, was obtained. The material showed slight decomposition after standing several days exposed to the air.

0.2364 grams substance; 0.2441 g. AgBr.

Calc. for $C_{14}H_{10}O_2Br_2$, Br, 43.24%;

Found, Br, 43.90%.

Benzoyl Bromide and Para-brombenzaldehyde.

Para-brombenzaldehyde was prepared from para-bromtoluene by brominating the methyl group and then hydrolyzing with calcium carbonate just as was done in the preparation of ortho-brombenzaldehyde. The yield was 43 grams of aldehyde from 50 grams of bromtoluene.

When 3 grams (1 mole) benzoyl bromide was added to 3 grams (1 mole) para-brombenzaldehyde, the aldehyde went into solution in ten minutes and the solution became cold. In three hours crystals began to separate and the entire mass had soon crystallized. It was washed with a little dry ether, then with petrol

ether and finally recrystallized from ligroin. The yield was nearly theoretical. The white crystals melted at 110° (uncorr) and showed only slight decomposition after standing in the air for ten hours.

0.1978 grams substance; 0.2023 g. AgBr.

Calc. for $C_{14}H_{10}O_2Br_2$, Br, 43.24%.

Found, Br, 43.54%.

Benzoyl Bromide and Para-nitrobenzaldehyde.

3.9 grams (1 mole) para-nitrobenzaldehyde was added to 4.8 grams (1 mole) benzoyl bromide. The aldehyde went into solution slowly. After standing a day the entire mass had solidified. After recrystallization from ligroin the material melted at 89-90°. Neither ligroin nor any of the common solvents were perfectly satisfactory for the crystallization, however. The solid appeared to be quite stable in the air. No analysis was made.

Benzoyl Bromide and Anisaldehyde.

The reaction between molecular amounts of benzoyl bromide and anisaldehyde went vigorously with the evolution of heat. The solution turned purple but the product did not crystallize; at the end of three months crystals of impure benzoic acid had formed.

Benzoyl Bromide and Nitro-anisaldehyde.

Nitro-anisaldehyde was prepared by the nitration of anisaldehyde below 0° according to the method of Einhorn and Grabfield[19] and of Wörner[20]. After several recrystallizations from dilute alcohol, the nitro-anisaldehyde melted at 72-73°. The melting point

given by Einhorn and Grabfield is 83.5° while that given by Wörner is 72°. The yield of pure product from 15 grams anisaldehyde was 8 grams.

4.1 grams (1mole) nitro-anisaldehyde was added to 4.15 grams (1 mole) benzoyl bromide and mixed. Some of the nitro- anisaldehyde went into solution and the mixture became cool. In two hours the solid had all dissolved and in another hour the material suddenly solidified. The solid was washed with a little dry ether to remove benzoyl bromide and anisaldehyde. 7 grams of light yellow solid was thus obtained which was recrystallized from hot ligroin. White crystals, m.p. 101-102° (uncorr) were obtained which decomposed slowly in the air but when sealed in glass tubes underwent little change.

0.1630 grams substance; 0.0817 g. AgBr.

Calc. for $C_{15}H_{12}O_5N\ Br$, Br, 21.86%

Found, Br, 21.33%.

Benzoyl Bromide and Salicylaldehyde.

When equivalent quantities of the two liquids were mixed, a very vigorous reaction set in with the evolution of a large amount of hydrogen bromide; the liquid became red. The hydroxyl group is evidently attacked by the benzoyl bromide.

Benzoyl Bromide and Methyl-salicylaldehyde.

The methyl ether of salicylaldehyde was prepated by the action of dimethyl sulfate on the sodium salt of salicylaldehyde according to the method of Katschalowsky and Kostanecki[21] and

purified by distillation. 24 grams of salicylaldehyde yielded 10 grams of the methyl ether boiling at 225-27°(uncorr).

8 grams (1 mole) methyl-salicylaldehyde was added to 10.9 grams (1 mole) benzoyl bromide. The mixture soon became quite hot and the reaction was complete in about an hour giving an orange colored, viscous liquid. Most of it solidified on standing. The solid was filtered off on a Büchner funnel and washed successively with petrol ether and a little dry ethyl ether. This left a perfectly white solid which decomposed in less than ten seconds, turning yellowish green and giving off fumes of hydrobromic acid. The material melted roughly at 50° but decomposition was too rapid for either an accurate melting point or an analysis.

Benzoyl Bromide and Vanillin.

Equivalent amounts of benzoyl bromide and vanillin reacted very vigorously giving a green substance which could not be crystallized, and from which nothing could be isolated. It is probable that the hydroxyl group of the vanillin was attacked by the benzoyl bromide.

Benzoyl Bromide and Methyl-Vanillin.

The methyl-vanillin was prepared by the action of dimethyl sulfate on the sodium salt of vanillin by the method of Rosenmund.[22]

When molecular quantities of methyl-vanillin and benzoyl bromide were mixed. The reaction began immediately and the solution soon became quite hot. After standing for some time the material turned to a green sticky solid which was recrystallized from petrol

ether. Very unstable white crystals were obtained which melted at 100°. They turned green in a few seconds in the air and also when covered with petrol ether or ligroin.

Benzoyl Bromide and Acetvanillin.

The acetvanillin was made by shaking the sodium salt of vanillin with an ether solution of acetic anhydride according to the method of Tiemann and Nagai[23]. 10 grams vanillin yielded 8 grams acetvanillin, m.p. 75-76° (uncorr.).

3 grams (1 mole) acetvanillin was added to 2.86 grams (1 mole) benzoyl bromide. A thick mush was formed but no heat effect was noticeable. In several hours the material had set to a very hard yellow solid which fumed in the air, slowly giving acetvanillin and benzoic acid. It was recrystallized four times from ligroin. 4 grams of white crystals were obtained, m.p. 102-103°. They decomposed slowly in the air.

0.2111 grams substance; 0.1056 g. AgBr.

Calc. for $C_{17}H_{15}O_4Br$, Br, 21.12%

Found, Br, 21.27%

Benzoyl Bromide and Terephthalic Aldehyde.

216 grams (1 mole) terephthalic aldehyde was added to 7.2 grams (2 moles) benzoyl bromide. No heat effect was noticeable but in a few hours the material had set to a hard gray solid. This was washed with dry ether and 9 grams of almost white crystals was obtained. The material was insoluble in many of the common organic solvents; it was recrystallized from hot ethylene

chloride, altho this solvent was not altogether satisfactory; m.p. 153-162°.

0;2135 grams substance; 0.1736 g. AgBr.

Calc. for $C_{22}H_{16}O_4Br_2$, Br, 31.75%.

Found, Br, 34.60%.

Benzoyl Bromide And Piperonal.

When molecular amounts of benzoyl bromide and piperonal were shaken together, the piperonal soon went into solution, and on standing, the liquid became green and viscous; some crystals separated after several days. These were filtered off and washed with absolute ether, which gave perfectly white, but unstable crystals, m.p. about 105-110°. The compound was recrystallized from ligroin but decomposed at once in the air, changing to a blue mush. No analysis could therefore be made.

Benzoyl Bromide And Brom-piperonal.

When 3.8 grams (1 mole) brom-piperonal was treated with 3.8 grams (1¼ mole) benzoyl bromide, the mixture formed red mush which did not change in appearance after standing several days. The solid was purified by washing with ether and recrystallizing from ligroin. This gave white crystals, m.p. 108-113°. Further crystallization did not change the melting point, as some decomposition always accompanied the crystallization. The crystals slowly decomposed in the air.

0.1956 grams substance; 0.1713 g. AgBr.

Calc. for $C_{15}H_{10}O_4Br_2$, Br, 38.64%

Found, 37.27%.

Benzoyl Bromide and Furfural.

A very vigorous reaction took place when equivalent quantities of benzoyl bromide and furfural were mixed; the product was a charred mass from which nothing could be isolated. Similar results were obtained when the reaction was carried on in ether solution, and also when a mixed ethyl ether and petrol ether solution was used.

Benzoyl Bromide And Heptaldehyde.

When molecular amounts of heptaldehyde and benzoyl bromide were mixed, the liquid turned cloudy and warmed up. In a few hours crystals had separated, which proved to be benzoic acid. No other solid could be obtained, and the material was not further investigated.

Benzoyl Bromide And Chloral.

When equivalent quantities of benzoyl bromide and chloral were mixed, no reaction was apparent, even after standing for several months; hence the investigation of the reaction was abandoned.

II. ADDITION REACTIONS OF OXALYL BROMIDE.

Oxalyl Bromide And Benzaldehyde.

The addition product of oxalyl bromide and benzaldehyde was obtained in very good yield (90%) when prepared either in the presence or absence of a solvent. The product was more easily purified, however, if the reaction was carried on in a solvent.

Staudinger and Anther[13] found that petrol ether is very satisfactory for this purpose. The product, after recrystallization from carbon bisulfide, was unstable in the air, gradually giving off hydrobromic acid but it required five minutes boiling with water to decompose it completely into benzaldehyde, hydrobromic acid, carbon monoxide, and carbon dioxide.

Oxalyl Bromide And Ortho-brombenzaldehyde.

Ortho-brombenzaldehyde was prepared as follows:- 50 grams (1 mole) ortho-bromtoluene was put into a flask fitted to a reflux condenser, and heated in an oil bath to 90°. 94 grams (2 moles bromine was slowly added in the sunlight; after half of the bromine had been added, decolorization took place more slowly and the temperature was gradually raised to 150°. The reaction was complete in four hours. The product was added to 500 cc. water and 150 grams of powdered calcium carbonate in a 3- liter flask, and refluxed seven hours and finally steam distilled. The aldehyde was taken up from the distillate with ether, which was then evaporated off and the aldehyde treated with an excess of sodium bisulfite solution. Water was added until all but a small amount of sticky material had dissolved; this was filtered off, the filtrate made alkaline with sodium carbonate, and the aldehyde distilled over with steam. Yield, about 80% of theory.

To 3 grams (2 moles) of the aldehyde, 2 grams (1½ moles) oxalyl bromide was added and the material allowed to stand. In tenhours the material began to solidify, and the reaction was soon complete. The product was washed with a little dry ether, and re-

crystallized from hot ligroin. Practically a theoretical yield of stable white crystals, m.p. 140° (uncorr.) was obtained.

0.2107 grams substance; 0.2696 g. AgBr.

Calc. for $C_{16}H_{10}O_4Br_4$, Br, 54.60%

Found, Br, 54.45%

Oxalyl Bromide And Cinnamic Aldehyde.

To 6.6 grams (1 mole) freshly distilled cinnamic aldehyde in a small frask connected to a reflux, 12 grams (1 mole) oxalyl bromide was gradually added. The liquid boiled and in a short time had become very brown and viscous and in two hours had solidified to a gray solid. This was washed with absolute ether, which removed the colored material and left perfectly white crystals, m.p. 85-86° with decomposition. The yield was only 8 grams, due to the solubility of the crystals in the ether. A better yield was obtained by recrystallizing the impure material from benzene, but the crystals thus obtained decomposed more quickly than when they were merely washed with ether. In either case, the material decomposed quickly, even when sealed in glass tubes.

0.2576 grams substance; 0.2056 g. AgBr;

0.1976 grams substance; 0.3649 g. CO_2, 0;0616 g. H_2O.

Calc. for $C_{20}H_{16}O_4Br_2$, Br, 33.33%; C, 50.00%; H, 3.33%.

Found, Br, 33.57%; C, 50.36%; H, 3.46%.

Oxalyl Bromide And Anisaldehyde.

11 grams (2 moles) anisaldehyde was dissolved in 50 cc. absolute ether and 10 grams (1 mole) oxalyl bromide added. Heat

was evolved by the reaction, and crystals soon separated from the solution. After standing two days the crystals were filtered off and washed with a litter ether. Yield, 21 grams, m.p. about 66°, with decomposition. The material was very unstable and decomposed quickly in the air turning dark and giving off gases. It could not be recrystallized from petrol ether and higher boiling solvents caused it to decompose. The analysis was made on a fresh sample.

0.2800 grams substance; 0.2163 g. AgBr.

Calc. for $C_{18}H_{16}O_6Br_2$, Br, 34.18%;

Found, Br, 32.87%.

Oxalyl Bromide And Nitro-anisaldehyde.

When 1.5 grams (2 moles) nitro-anisaldehyde was added to 1.5 grams (1½ mole) oxalyl bromide, the reaction went fairly rapidly with the evolution of some heat. A brown liquid was obtained, which crystallized to a brown solid after four days. It was washed with dry ether and recrystallized from a mixture of one volume of benzene and four volumes of ligroin. The white crystals melted at 116-118° (uncorr.). They were quite stable in the air undergoing no appreciable decomposition after standing a day. They were soluble in chloroform and benzene, insoluble in ligroin or petrol ether.

0.2206 grams substance; 0.1452 grams AgBr.

Calc. for $C_{18}H_{14}\Phi_{10}N_2Br_2$, Br, 27.68%.

Found, Br, 28.02%.

Oxalyl Bromide And Ortho-nitrobenzaldehyde.

To 7 grams (2 moles) Ortho-nitrobenzaldehyde, a slight excess over 1 mole oxalyl bromide was added. The solution became cool and the aldehyde soon went into solution. In an hour the material had changed to a red solid which was washed with a little absolute ether. This removed the red color and left a perfectly white solid melting at 158-162^{0} (uncorr.) without decomposition. The material was quite stable in the air showing no decomposition after standing two days. Yield, 6 grams.

0.2094 grams substance; 0.1616 g. AgBr.

Calc. for $C_{16}H_{10}O_8N_2Br_2$, Br, 31.55%;

Found, Br, 32.80%.

Oxalyl Bromide And Meta-nitrobenzaldehyde.

When 0.8 grams (2 moles) meta-nitrobenzaldehyde was added to 0.65 grams (slightly over 1 mole) oxalyl bromide, the aldehyde gradually went into solution but no heat effect was noticeable. The material obtained was a brown viscous mass which did not solidify, but when a little dry ether was added it immediately changed to a yellow crystalline solid. This was well washed with dry ether to remove nitro-benzaldehyde and oxalyl bromide;yield 1.2 grams. The material was purified by dissolving it in hot chloroform and adding six times its volume of petrol ether and cooling. The crystals readily came out of solution, light yellow in color, m.p. 128-129° (uncorr.). The crystals were comparatively stable in the air but decomposed after standing exposed to the air for several days.

0.2240 grams substance; 0.1673 g. AgBr;

Calc. for $C_{16}H_{10}O_8N_2Br_2$, Br, 30.88%;

Found, Br, 31.80%.

Oxalyl Bromide And Para-nitrobenzaldehyde.

When equivalent amounts of oxalyl bromide and para-nitrobenzaldehyde were mixed, part of the aldehyde went into solution without any heat effect. The material was heated to 50° for a few minutes which caused all the aldehyde to go into solution. On cooling, an orange colored solid was obtained, which, after washing with ether left a white solid; this was found to be unchanged nitro-benzaldehyde. No reaction had taken place between the aldehyde and the oxalyl bromide.

Oxalyl Bromide And Piperonal.

7 grams (2 moles) of piperonal was dissolved in about 25 cc. absolute ether, and 5 grams (1 mole) of oxalyl bromide added in portions. A large amount of heat was evolved and gases were given off. In five minutes the material had solidified to a slightly yellow solid which was washed with absolute ether. This left 11.5 grams of white solid, melting at 65-68°. It was quite unstable in the air, quickly turning yellow. After two crystallizations from hot chloroform, it melted at 81-83° but when it was dissolved in hot chloroform, it decomposed somewhat giving off hydrogen bromide. Cold water decomposed the solid quickly, giving piperonal and hydrobromic acid.

0.2092 grams substance; 0.1534 g. AgBr.

Calc. for $C_{16}H_{12}O_8Br_2$, Br, 31.01%; Found, Br, 31;20%.

Oxalyl Bromide And Vanillin.

2.7 grams ($1\frac{1}{4}$ mole) oxalyl bromide was gradually added to 3 grams (2 moles) of vanillin dissolved in 75 cc. dry ether. The reaction took place at once with the evolution of heat, and white crystals quickly separated from the solution. The reaction was complete in five to ten minutes and the crystals were filtered off; m.p. 93-5°; yield 90% of theory.

0.2110 grams substance; 0.1551 g. AgBr.

Calc. for $C_{18}H_{16}O_8Br_2$, Br, 30;77%;

Found, Br, 31;30%.

Oxalyl Bromide And Acetvanillin.

When 2 grams (2 moles) acetvanillin was added to 1.25 grams (1 mole) oxalyl bromide, the acetvanillin quickly went into solution and the mixture warmed up. After standing a few hours, the material set to a yellow solid; the yield was practically theoretical. The substance was soluble in hot chloroform and benzene, insoluble in ligroin and petrol ether. It was purified by dissolving it in hot chloroform and precipitating it out by adding petrol ether. After two such recrystallizations, the white crystals melted at 142-143° with decomposition. The material was fairly stable, undergoing only slight decomposition after standing in the air several hours.

0.1049 grams substance; 0;0650 g. AgBr.

Calc. for $C_{22}H_{20}O_{10}Br_2$, Br, 26.49%;

Found, Br, 26.37%.

Oxalyl Bromide And Methyl-salicylaldehyde.

A vigorous action took place when 4 grams (2 moles) methyl-salicylaldehyde was mixed with 3.5 grams (1 mole) oxalyl bromide and a large amount of heat was evolved. The material obtained was hard to purify, hence a new reaction was begun in 10 cc. dry ether solution. Within a few minutes after the substances were mixed, white crystals began to deposit out of the ether, and at the end of ten hours, 7 grams of crystals had separated. The substance was soluble in chloroform and benzene, but insoluble in ligroin or petrol ether; it was purified by dissolving it in hot chloroform and addind six times its volume of petrol ether. On cooling, white crystals were obtained which melted at 99° with decomposition. The crystals were unstable and after standing in a stoppered tube for a day, they had nearly entirely decomposed.

0.2177 grams substance; 0.1738 g. AgBr.

Calc. for $C_{18}H_{16}O_6Br_2$, Br, 32.78%;

Found, Br, 33.97%.

Oxalyl Bromide And Furfural.

2.67 grams (2 moles) furfural was added to 20 cc. petrol ether, and then just enough dry ethyl ether added to take the furfural into solution. When 3 grams (1 mole) oxalyl bromide was added, the solution warmed up and soon white crystals deposited on the walls of the flask; in about an hour the reaction appeared to be complete. The crystals were unstable and soon turned dark on standing or when heated to 40°. After several recrystallizations from ligroin, the melting point was 76-77°. The crystals

were quickly dried on a clay plate and the sample weighed out and sealed up in a bomb tube.

0.2287 grams substance; 0.2117 g. AgBr.

Calc. for $C_{12}H_8O_6Br_2$, Br, 39.41%;

Found, Br, 39.42%.

Oxalyl Bromide And p-dimethylaminobenzaldehyde.

When a slight excess over 1 mole of oxalyl bromide was added to an ether solution of 2 moles of the aldehyde, a vigorous reaction took place; it was complete in a few minutes, giving practically a theoretical yield of green solid, unsoluble in ether, and unstable in air. When the moist material was exposed to the air or heated, it soon turned from green to an orange-red solid, and then to a red liquid. The solid was washed with dry ether and dried on a clay plate; in the dry state it was fairly stable, showing only a slight change to the yellow color in half an hour. In six hours it had entirely changed to the red liquid. The green solid melted at 102-3°, with decomposition. It was soluble in cold benzene, ligroin, and chloroform, insoluble in dry ether. In chloroform it gave a yellow solution. It was the impure hydrobromide of para-dimethylaminobenzalbromide. Staudinger[24] obtained an analogous compound by the action of oxalyl bromide on the same aldehyde.

0.2026 grams substance; 0.2668 g. AgBr.

Calc. for $C_{20}H_{22}O_4N_2Br_2$, Br, 31.13%.

Calc. for dimethylaminobenzalbromide hydrobromide, $C_9H_{12}NBr_3$,

Br, 64.2% Found Br, 56.02%

III. ADDITION REACTIONS OF OTHER ACID HALIDES.

Para-nitrobenzoyl Bromide And Benzaldehyde.

The para-nitrobenzoyl bromide was prepared by the method of Adams and Ulich[25] as follows: 30 grams oxalyl bromide was dissolved in 40 cc. dry benzene in a flask fitted to a reflux, and 20 grams dry sodium salt of p-nitrobenzoic acid gradually added during the course of an hour. After heating four hours on the water bath, the sodium bromide was filtered off and petrol ether added to the filtrate. The acid bromide comes out in yellow needles and additional amounts can be obtained from the mother liquors. The crystals were redissolved in a little hot benzene and reprecipitated with petrol ether. Yield, 10 grams; m.p. 63-64°.

When 3.4 grams (1 mole) of the acid bromide was mixed with 1.6 grams (1 mole) benzaldehyde, the mixture became cool and in ten minutes the acid bromide had all gone into solution. As soon as solution had taken place, the solution warmed up slightly and the material began to solidify, In fifteen minutes from the time of mixing, the entire mass had crystallized to a yellow solid. This was washed with a little dry ether; the yield was practically quantitative. By recrystallizing from hot ligroin, very light yellow colored crystals were obtained, m.p. 132° (uncorr). The solid was quite stable and showed only slight decomposition after standing 3 days in the air.

0.2346 grams substance; 0.1323 g. AgBr;

Calc. for $C_{14}H_{10}O_4NBr$, Br, 23.81%;

Found, Br, 24.00%.

Oxalyl Chloride And Vanillin.

When 2 moles of vanillin was treated with 1 mole of oxalyl chloride, the reaction went so vigorously that the product was a charred mass and could not be purified. The reaction went slowly in ether solution but the product obtained was the same as before.

Acetyl Chloride And Benzaldehyde.

No reaction was at first apparent when equivalent amounts of benzaldehyde and acetyl chloride were mixed, but the liquid gradually warmed up on standing and became yellow. At the end of a half hour it had become quite hot. After the reaction had died down, it was heated on the water bath for a short time and allowed to cool. No crystals came out when the material was cooled in a freezing mixture, hence it was distilled under 20 mm. pressure. When the heating was begun, the vacuum varied from 50 to 100 mm., the compound apparently breaking up into acetyl chloride and benzaldehyde, which made up the low boiling fractions. About a third of the total amount of material distilled at 100-105^{0} at 20 mm. This fraction had the odor of both acetyl chloride and benzaldehyde. It was insoluble in water with which it slowly reacted with the evolution of heat, giving benzaldehyde.

10 grams of the material was treated in ether solution with 1 mole silver benzoate with which it slowly reacted. From the ether solution an oil was obtained which was washed with sodium bisulfite solution and then dried. Only 0.5 gram of viscous yellow liquid which could not be crystallized was obtained.

Benzoyl Chloride And Brom-methylvanillin.

Brom-vanillin was made by passing a stream of air containing bromine through an alcohol solution of vanillin, according to the method of Tiemann and Haarmann[26], the yield was theoretical. The ethyl ether of brom-vanillin was prepared with more difficulty. 21 grams brom-vanillin was dissolved in 150 cc. of a 2.5% solution of sodium hydroxide and warmed until nearly all the solid had dissolved. 14 grams dimethyl sulfate was then added in portions with vigorous shaking; more sodium hydroxide solution was then added until the solution became colorless. 11 grams more dimethyl sulfate was added and the solution heated another half hour. After quickly cooling in ice, the solid was filtered off with suction and boiled with 300 cc. water to remove sodium salts. The solid was filtered off and recrystallized from dilute alcohol. The crystals melted at 56-58° to give a milky liquid, which cleared up rather sharply at 105°.

3 grams (1 mole) brom-methylvanillin was mixed with 1.75 grams (1 mole) benzoyl bromide and soon went into solution. After standing for a week, the material had changed to a thick mush, which was washed with a little dry ether and recrystallized from ligroin. The yield was less than 1 gram. m.p. 158-160°.
0.0732 grams substance; 0.0640 grams AgCl + AgBr.
Calc. for $C_{16}H_{14}O_4ClBr$, AgCl + AgBr, 0.0628 grams.

Benzoyl Chloride And Brom-piperonal.

The brom-piperonal was prepared by the method of Oelker[27]

3 grams (1 mole) brom-piperonal was added to 1.85 grams (1 mole)

benzoyl chloride; most of the material had solidified after standing a week. The solid was washed with a little ether and recrystallized several times from ligroin; m.p. 97-102°. The crystals were stable in the air for a short time, but turned gray after standing several hours; this also occured when they were tightly stoppered.

0.0784 grams substance; 0.0711 g AgCl+ AgBr.

Calc. for $C_{15}H_{10}O_4ClBr$, AgCl + AgBr, 0.0702 g.

Benzaldehyde And Ortho-nitrobenzoyl Chloride.

No apparent reaction took place when 5 grams (1 mole) ortho-nitrobenzoyl chloride was mixed with 3 grams (1 mole) benzaldehyde. The container was scratched occasionally, and in a week the entire mass had set to a pink solid. The sticky material was removed by boiling with petrol ether, which also removed the pink color and left a yellowish green solid. This was recrystallized from hot ligroin. Yield, 5 grams. The crystals were white, m.p. 81-82° (uncorr.).

0.1930 grams substance; 0.0925 g. AgCl.

Calc. for $C_{14}H_{10}O_4N$ Cl, Cl, 12.18%;

Found, Cl, 11.88%.

Benzaldehyde And Meta-nitrobenzoyl Chloride.

5 grams (1 mole) meta-nitrobenzoyl chloride was added to 3 grams (1 mole) benzaldehyde. After standing three months, crystals began to come out, and by scratching the tube, the entire mass was soon crystallized. If the mixture was inoculated with a crystal of the addition product, it could be caused to solidify

in five or six days. The material was soluble in cold ether and ethylene chloride, insoluble in petrol ether. It was recrystallized several times from ligroin. Yellow crystals were obtained in practically theoretical yield, m.p. 87-88^{0}.

0.2054 grams substance; 0.1024 g. AgCl.

Calc. for $C_{14}H_{10}O_4N$ Cl, Cl, 12.18%;

Found, Cl, 12.35%.

Benzaldehyde And Para-nitrobenzoyl Chloride.

When 5 grams (1 mole) para-nitrobenzoyl chloride was added to 3 grams (1 mole) benzaldehyde, the liquid became cool and in a day most of the acid chloride had gone into solution. After five days, all the material had solidified. After several recrystallizations from ligroin, the yellow crystals melted at 118-118.5^{o}. They were quite stable in the air and also in water. Even cold 10% sodium carbonate solution did not react readily with the material.

0.1858 grams substance; 0.0946 g. AgCl.

Calc. for $C_{14}H_{10}O_4N$ Cl, Cl, 12.18%;

Found, Cl, 12.59%.

Halogen Substituted Acid Chloride and Benzaldehyde.

Benzaldehyde did not react with para-chlorbenzoyl chloride, para-brombenzoyl chloride, or ortho-brombenzoyl chloride, even after standing at 30° for several months. A small amount of dry zinc chloride had no effect on the mixture of benzaldehyde and ortho-brombenzoyl chloride, although the mixture was left in contact with the zinc chloride for several weeks.

Toluene-sulfonylchloride And Benzaldehyde.

When equivalent quantities of ortho-toluene-sulfonylchloride and benzaldehyde were mixed, a small part of the sulfonylchloride went into solution and the liquid became red. The remainder of the acid chloride would not go into solution except when heated, and when the solution cooled it again separated out. No reaction at all had taken place after standing ten months.

IV. STRUCTURE OF THE ADDITION COMPOUNDS.

Action Of Silver Benzoate On The Addition Product Of Benzoyl Bromide And Benzaldehyde.

The addition product of benzaldehyde and benzoyl bromide was made by mixing equivalent quantities of the two substances[1]; after standing for a few days, the material solidified and was recrystallized from petrol ether. The substance crystallized in large white crystals which were unstable in the air.

20 grams (1 mole) of the addition product was dissolved in 300 c.c. absolute ether, and an excess of silver benzoate added. The reaction began immediately, causing the ether to boil; silver bromide was formed. When the reaction was complete, the ether solution was filtered off and evaporated, leaving 16 grams of a slightly yellow liquid which could not be crystallized. It was accordingly distilled under 31 mm. pressure and gave benzaldehyde and benzoic anhydride; hence the compound cannot be distilled without decomposition. Accordingly, some benzylidene dibenzoate was prepared from benzoic anhydride and benzaldehyde

according to the method of Wegscheider and Späth[16]. After three crystallizations out of petrol ether, the crystals melted at 62-63° (Wegscheider and Späth give 61-62°). When some of these crystals were used to inoculate the liquid obtained by the action of silver benzoate on the condensation product of benzoyl bromide and benzaldehyde, the product quickly crystallized, and a mixed melting point showed the two substances to be the same. Analysis of the product obtained from silver benzoate and the addition product which had stood in a vacuum dessicator for a day, gave C, 78.0%; H, 5.62%. Theory for benzylidene dibenzoate, C, 75.90%; H, 4.82%. After heating some of the material at 100° for three hours, a second analysis gave C, 76.7%; H, 5.3%. The remainder of the material from which this analysis had been made was heated for eight hours at 100° and the results of the third analysis were: 0.1736 grams substance; 0.4832 grams CO_2; 0.0788 grams H_2O. C, 75.91%; H, 5.04%.

Similar results were obtained with the benzylidene dibenzoate obtained from benzaldehyde and benzoic anhydride. It thus seems that some petrol ether of crystallization, or petrol ether held in some other manner, is held by the benzylidene dibenzoate. The difference between the first and last analyses corresponds to about two molecules of pentane.

The addition compound obtained from benzaldehyde and benzoyl bromide is therefore brombenzylbenzoate, C_6H_5-CHBr-O-CO-C_6H_5.

Brombenzylbenzoate And Silver Acetate.

A slight excess of silver acetate was added to an ether

solution of brombenzylbenzoate; the reaction began at once and in less than anhour was entirely complete. The ether solution was filtered off and the ether evaporated, leaving a clear almost colorless, syrupy liquid which solidified to a white solid when the walls of the container were scratched. Yield, 16 grams from 13 grams brombenzylbenzoate. After several crystallizations from ligroin, the melting point remained constant at 71-72°.

0.2138 grams substance; 0.5556 grams CO_2, 0.1039 grams H_2O.

Calc. for $C_{16}H_{14}O_4$, C, 71.11%; H, 5.19%;

Found, C, 70.86%; H, 5;40%.

Brombenzylbenzoate And Silver Cyanide.

Brombenzylbenzoate in ether solution reacted only very slightly with silver cyanide and no reaction product could be isolated.

Brombenzylbenzoate And Silver Propionate.

17.5 grams (>1 mole) silver propionate reacted readily with an ether solution of 30 grams (1 mole) brombenzylbenzoate; the ether solution was evaporated off and evaporated, leaving 26 grams of an orange colored liquid which did not crystallize and decomposed when distilled in vacuo.

Brombenzylbenzoate And Silver Chloracetate.

23 grams brombenzylbenzoate was dissolved in 100 c.c. absolute ether and 16 grams of the silver salt of chloracetic acid added. The reaction began at once and yielded 21 grams of yellow

liquid which could not be crystallized.

Action of Bromine on Benzylbenzoate.

The reaction of bromine in the sunlight was tried in an attempt to synthesize brombenzylbenzoate, but benzoic acid was the only solid which could be obtained.

Action of Bromine on Benzyl Oxalate.

An attempt was made to synthesize the addition product of oxalyl bromide and benzaldehyde, by the action of bromine on benzyl oxalate. The reaction was carried on with and without a solvent, and in the presence and absence of sunlight. The compound desired was not obtained, however. Benzyl bromide and benzoic acid were identified among the products obtained.

The Action of Silver Acetate on the Addition Product of Benzaldehyde and Para-nitrobenzoylchloride.

The addition product between p-nitrobenzoylchloride and benzaldehyde was prepared as has been described. Ten grams of the recrystallized product were dissolved in hot absolute ether and ten grams silver acetate added. The reaction went slowly, but on standing, a white precipitate came out and was filtered off. The ether was evaporated off, leaving 10 grams of a yellow viscous liquid which slowly solidified when cooled. Yield,6 grams. The material was soluble in most organic solvents, but insoluble in ligroin. It was dissolved in a little absolute ether, some petrol ether added, and the solvent allowed to evaporate spontaneously. The yellow solid melted at 63-67°.

0.1672 grams substance; 7.75 c.c. N_2 at 20° and 723.5mm. corrected barometric pressure.

Calc. for $C_{16}H_{13}O_6N$, 4.44%;

Found, 4.76%.

Benzoic-acetic Anhydride And Benzaldehyde.

In an attempt to synthesize the compound obtained by the action of silver acetate on brombenzylbenzoate, the method of Wegscheider and Späth was tried, whereby benzoic-acetic anhydride was heated with benzaldehyde in the presence of a small amount of sulfuric acid. The benzoic-acetic anhydride was prepared by the action of acetyl chloride on a chloroform solution of benzoic acid and pyridine[28]. However, the product obtained was not benzylidene benzoate-acetate, but benzylidene dibenzoate, just as in the case of benzoic anhydride and benzaldehyde.

Benzoic-para-nitrobenzoic Anhydride And Benzaldehyde.

The method of Wegscheider and Späth was also tried in an attempt to synthesize benzylidene benzoate-p-nitrobenzoate. Benzoic-p-nitrobenzoic anhydride was made by heating equivalent quantities of the sodium salt of nitrobenzoic acid and benzoyl chloride several hours on the steam bath. The powdered solid was washed with a 10% solution of sodium carbonate, then with water, and dried on filter paper. The yellow solid was purified by dissolving it in hot chloroform and adding petrol ether until a turbidity appeared, then cooling. The solid very readily crystallized out. It melted at 127-133°.

To 5 grams of the anhydride, 1 gram benzaldehyde and 8 drops

concentrated sulfuric acid were added and the mixture heated to 110-120° for an hour. When the resulting black liquid was treated with potassium hydroxide solution, it gave a tarry solid which could not be purified.

The above two cases seem to indicate that the method of Wegscheider and Späth cannot be used in the case of mixed anhydrides.

V. REACTIONS OF THE ADDITION COMPOUNDS.

Brombenzylbenzoate And Ammonia.

Dry ammonia gas was led into an ether solution of 20 grams brombenzylbenzoate until no more white solid precipitated out. The solid was filtered off and the ether evaporated from the filtrate; 6 grams benzaldehyde were thus obtained. The solid, weighing 13 grams, was a mixture of ammonium bromide and benzamide. It was extracted with hot benzene; when the solution cooled, benzamide separated out.

Brombenzylbenzoate And Aniline.

When equivalent quantities of brombenzylbenzoate and aniline were mixed, a great deal of heat was evolved by the vigorous reaction. A yellow solid was formed, which was stable in air and soluble in water. The solid material was extracted with ether, and pure benzoic acid was obtained from the ether extract. The ether-insoluble solid was analyzed for bromine.

0.2052 grams substance; 0.1504 grams AgBr.

Calc. for benzylidene-aniline hydrobromide, $C_{13}H_{12}NBr$, Br, 30.53%

Found, Br, 31.19%.

Some of the solid material was then treated with sodium hydroxide solution, and an oil came to the surface. When this was taken up in ether and the ether evaporated, the oil solidified. M.P. 45-48°, B.P. 300-305°.

0.2051 grams substance; 14.6 c.c. N_2 at 20° and 731 mm. corrected pressure.

Calc. for benzylidene aniline, $C_{13}H_{11}N$, N_2,7.74%.

Found, N_2,7.97%.

The other physical and chemical properties of the compound agree with those of benzylidene aniline.

In order to find the effect of temperature on the reaction, ether solutions of aniline and brombenzoylbenzoate were cooled and then mixed. No reaction took place at 0°, even after standing two hours. The solution was then removed from the ice bath and allowed to stand at room temperature; a yellow solid soon precipitated out. The ether was then allowed to evaporate spontaneously so that at no time did a noticeable heat reaction take place. On extracting with ether, benzoic acid was obtained, and the residue gave benzylidene aniline when treated with sodium hydroxide solution. The formation of benzylidene aniline is therefore not due to the rather high temperature observed when the substances are mixed.

Brombenzylbenzoate And Ortho-toluidine.

Equivalent quantities of brombenzylbenzoate and ortho-toluidine reacted very vigorously with the evolution of a large amount of heat. When the product was extracted with ether, benzoic

acid was obtained from the ether extract. The ether insoluble solid gave an oil when treated with sodium hydroxide solution. The oil boiled at 210-212° under 72 mm. but could not be crystallized at 0°.

0.2526 grams substance; 16.2 c.c. N_2 at 21° and 734.5 mm. corrected pressure.

Calc. for benzylidene toluidine, $C_{14}H_{13}N$, N_2, 7.2%;

Found, N_2 7.2%.

5.15 grams brombenzylbenzoate and 1.9 grams ortho-toluidine gave 3.3 grams benzylidene toluidine; theory, 3.45 grams.

Brombenzylbenzoate And Ethyl Alcohol.

An excess of ethyl alcohol was added to brombenzylbenzoate, which soon went into solution. After allowing to stand a day, the material was distilled in vacuo. Ethyl benzoate and benzaldehyde were the main constituents of the distillate although some halogen compounds which were not identified were also formed.

Brombenzylbenzoate And Dimethylaniline.

When two moles of dimethyl aniline was added to one mole brombenzylbenzoate, a great deal of heat evolved, and the product changed through yellow to a beautiful green sticky mass which did not solidify. It was soluble in water and a dye to cotton, closely resembling malachite green in appearance. On making alkaline it became colorless, but the color did not reappear when the alkaline solution was acidified.

Brombenzylbenzoate And Acetone.

Acetone reacted slowly with brombenzylbenzoate to give a black charred mass from which no compound could be isolated.

Brombenzylbenzoate And Metals.

Powdered zinc reacted very rapidly with an ether solution of brombenzylbenzoate to give an oil which consisted of a mixture of substances which could not be identified. Reduced copper reacted much more slowly and gave benzaldehyde and a very viscous colorless liquid which could not be crystallized, and was not further investigated.

Brombenzylbenzoate And Sodium Malonic Ester.

One equivalent of dry sodium malonic ester (ethyl) was added to an ether solution of one equivalent of brombenzylbenzoate, and allowed to stand. No reaction was apparent, hence the solution was boiled an hour, then filtered and the ether evaporated off. This left a yellow liquid which could not be crystallized. When sodium malonic ester (methyl) was used, similar results were obtained; the resulting product consisted partly of benzaldehyde.

VI. SUBSTITUTION REACTIONS OF OXALYL BROMIDE.

Preparation Of Oxalyl Bromide.

The oxalyl bromide which was used in the following reactions was prepared according to the directions of Staudinger[13] by passing four moles of dry hydrogen bromide through oxalyl chloride at

at 0°, the operation lasting from twelve to twenty hours. The material was then allowed to stand a day and finally distilled. Practically the entire amount came over at $103-105^{\circ}$. The yield was 145 grams from 100 grams of oxalyl chloride, or 85% theory. The hydrogen bromide used was generated by dropping bromine on red phosphorus and water, and leading the evolved gases over anthracene to remove bromine, and over calcium chloride and phosphorus pentoxide to remove water. The container for the oxalyl chloride was a tube about 5 cm. in diameter; this was connected to a good spiral condenser by a glass joint.

Oxalyl Bromide And Acetone.

When 10 grams (1 mole) of oxalyl bromide was added to 2.7 grams (1 mole) of dry acetone, the liquid quickly warmed up, gave off gases, and became yellow in color. At the end of 10 hours, the material had changed to a black viscous mass, which was distilled. The distillate came over from 80° to 100°, and the remainder of the material was left as a charred mass in the distilling bulb. The distillate was washed with water to remove acetone and oxalyl bromide, then dried and distilled. It came over at 100° to 120°, the yield being 4 grams. An accurate boiling point could not be obtained with such a small amount of material. The boiling point of 2,2-dibrompropane was found to be $114-114.5^{\circ}$ under 740 mm., by Linnemann[29].

Oxalyl Bromide And Methyl Ethyl Ketone.

5 grams (1 mole) methyl ethyl ketone was dissolved in 25 cc.

absolute ether, and 15 grams (1 mole) oxalyl bromide added. Heat and gases were evolved. The solution was allowed to stand over night, then refluxed 4 hours and finally distilled. At 100° the product became black, and yellow vapors were given off. Most of the distillate came over from 140° to 180°. Yield, 5.5 grams. The remainder of the material remained in the flask as a black residue. The distillate was washed with water, which removed the brown color and left a heavy yellow liquid. When distilled again, 3 grams of slightly flourescent material came over from 140° to 180°. The boiling point of 1,1,dibrombutane is 144-145°.

Oxalyl Bromide And Methyl Propyl Ketone.

10 grams (1 mole) oxalyl bromide was gradually added to 4 grams (1 mole) of methyl propyl ketone; the reaction began at once, with the evolution of some vapors and a considerable amount of heat. The liquid became yellow on standing, and lost the odor of oxalyl bromide. It was gently refluxed for an hour, which caused the liquid to turn black and tarry. On distillation, a few grams of brown liquid was obtained at 85-135°, and on fractionation most of this product came over at 110-130°. The odor was sweet and ethereal. 2,2,dibrompentane was probably formed by the reaction, and this when heated lost hydrogen bromide to give 2-brom, 1-pentene, whose boiling point is 122-123°, and whose odor corresponds to that of the material obtained.

Oxalyl Bromide And Benzophenone.

To 8 grams (1 mole) benzophenone in a small flask fitted to a reflux condenser, 10 grams (1 mole) oxalyl bromide was slowly

added. No heat or gas evolved, but the benzophenone quickly went into solution. In a short time, bubbles of gas began to come through the liquid, and the mixture was allowed to stand over night; it was then refluxed very gently for five hours, the liquid becoming brown and syrupy, and gases being given off. It was fractionated under 20 mm. pressure, and most of the material came over at 194°. The distillate was colorless, but on exposure to the air it turned red. When redistilled, it came over constant at 194-195°. Yield, 5 grams. The structure of the compound was proved by its reaction with aniline to give $(C_6H_5)_2{=}C{=}N{-}C_6H_5$, m.p. 108-109°.

Oxalyl Bromide And Benzalacetone.

When molecular amounts of oxalyl bromide and benzalacetone were mixed, the benzalacetone quickly dissolved and a vigorous reaction soon set in, so that the flask had to be cooled. The liquid turned to a black semi-solid, from which nothing could be isolated. A similar result was obtained when the reaction was carried on in ether solution.

Oxalyl Bromide And Dibenzalacetone.

11 grams (1 mole) oxalyl bromide was dissolved in 40 cc. absolute ether, and the solution gradually added to 12 grams (1 mole) dibenzalacetone. The ether boiled vigorously during the addition. When no further reaction was noticeable, the solution was gently refluxed for ten minutes, 60 cc. petrol ether added, and the solution cooled to below 0°. Yellow crystals soon began to come out; these were filtered off after a

half hour and dried on a clay plate. Yield, 10 grams. The material was easily recrystallized from a mixture of 19 cc. anhydrous ether and 30 cc. petrol ether. After three crystallizations, the melting point remained constant at 79-80°.(The melting point of $(C_6H_5CH=CH)_2=C=Br_2$ is given by Straus[30] as 91-92°) The solid was light yellow in color when dry, orange yellow when wet. On standing in the air, the moist material quickly became green around the edges; this change was not noticed when the material was dry.

0.2475 grams substance; 0.2475 grams AgBr.

Calc. for $(C_6H_5CH=CH)_2=C=Br_2$, Br, 42.32%;

Found, Br, 42.24%.

Oxalyl Bromide And Benzaldehyde.

When 10 grams (1 mole) oxalyl bromide was added to 5 grams (1 mole) of pure benzaldehyde, heat and gases were evolved, and the addition product[13] was first formed. The material was then gently warmed for several hours, causing gases to be evolved and the liquid to turn almost black. This was then distilled under 23-25 mm. pressure. Practically the entire amount came over at 130-135°. Yield, 12 grams. When redistilled, the liquid came over at 120-124° under 22 mm. pressure. Vorländer[17] found that benzal bromide, prepared in a different way, boils at 119-24° under 20-25 mm.

Oxalyl Bromide And Cinnamic Aldehyde.

An attempt was made to prepare cinnamyl-dibrom-methane by

the reaction of oxalyl bromide with cinnamic aldehyde at elevated temperature. It was found, however, that when the two substances were boiled together in the absence of a solvent, a charred mass was obtained; while in the presence of low boiling solvents such as ether or petrol ether, only the addition compound was formed. When a solution of the materials in ethylene chloride was refluxed, nothing besides a little cinnamic aldehyde and a large amount of charred material was obtained.

Oxalyl Bromide And Heptaldehyde.

When equivalent amounts of heptaldehyde and oxalyl bromide in ether solution were mixed, the reaction began at once and the solution turned black. The solution was allowed to stand four hours, the ether evaporated off, and the liquid washed with water. The brown liquid thus obtained was distilled under 30 mm. pressure but the temperature rose steadily from 190° to above 260°, and no definite boiling fraction could be obtained.

Oxalyl Bromide And Chromic Anhydride.

13 grams oxalyl bromide was added gradually to 5 grams of chromic anhydride. A reaction set in, heat being evolved and bromine vapors were given off. The mixture was refluxed eight hours. A red liquid which smelled of bromine colored the condenser all the way up. When the liquid was distilled, the temperature rose steadily up to 100°, and most of it came over at this temperature. The distillate was oxalyl bromide colored red by some bromine.

Similar results were obtained when oxalyl bromide and chromic

anhydride were heated to 125° in a bomb. If chromyl bromide was formed by the reaction, it is evidently so unstable that it decomposed as soon as it was formed.

Oxalyl Bromide And Benzoic Acid.

10 grams (1 mole) oxalyl bromide was added to 10.8 grams (2 moles) of benzoic acid. After standing at room temperature for two days, most of the benzoic acid had gone into solution. The remainder of the solid was filtered off and the filtrate distilled Most of it came over at 220-240°, and was found by hydrolysis to be benzoyl bromide. The yield was only three grams, however.

The experiment was repeated, using the same amounts of materials as before, but refluxing twenty hours. This gave two grams benzoyl bromide and three grams benzoic anhydride.

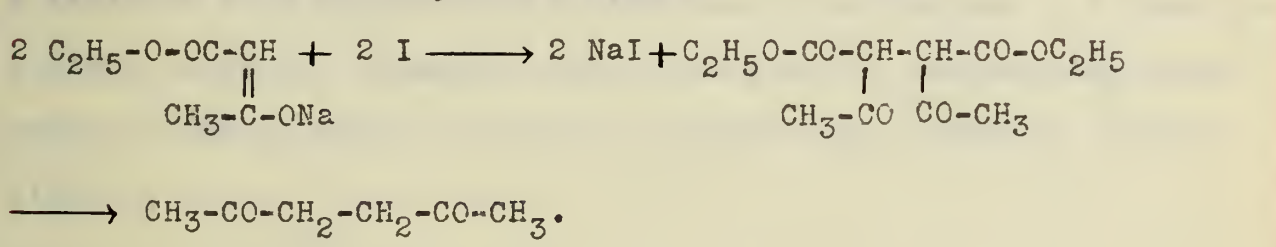
1-5 DIKETONES.

INTRODUCTION.

Two of the most general methods which have been used for the synthesis of diketones are : (1) the action of metallo-organic halides on the acid halides of dibasic acids[31]:

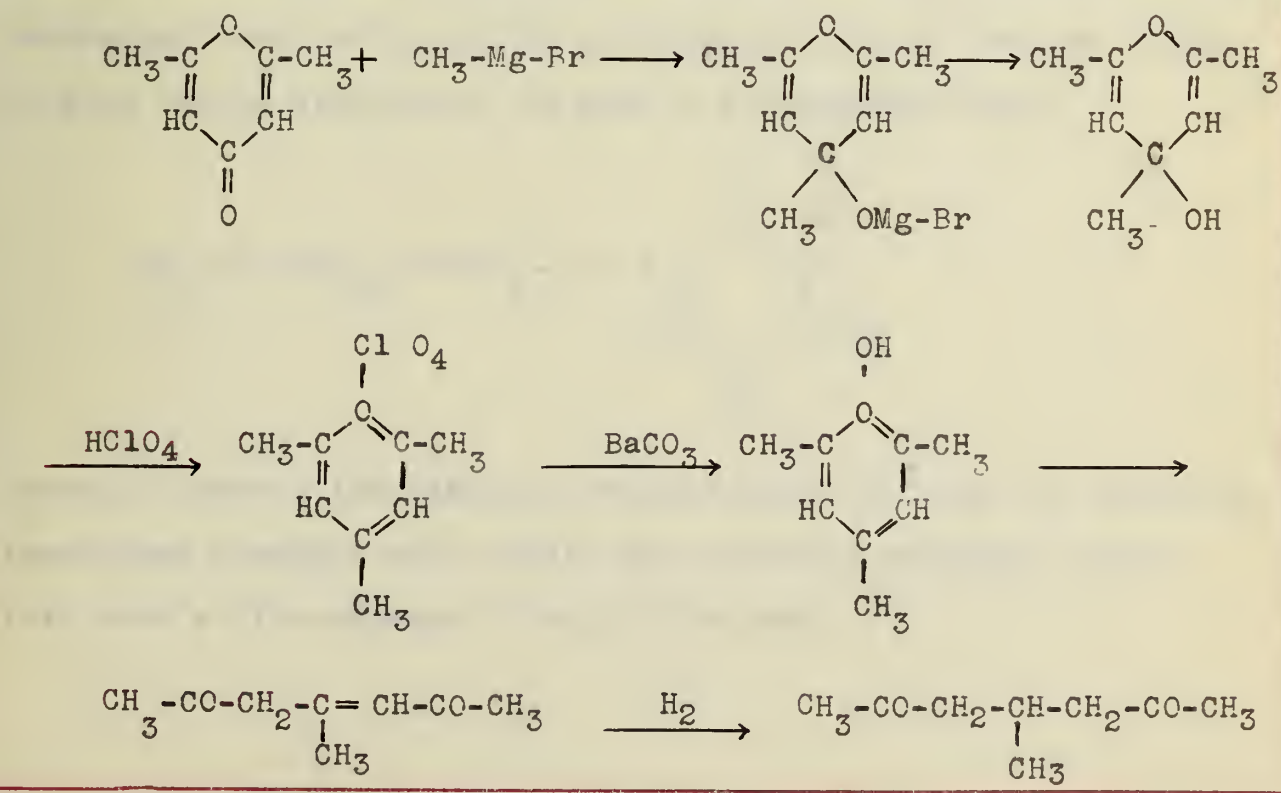
$$Cl\text{-}CO\text{-}(CH_2)_x\text{-}CO\text{-}Cl + R\text{-}Zn\text{-}I \longrightarrow R\text{-}CO\text{-}(CH_2)_x\text{-}CO\text{-}R + ZnI_2;$$

(2) the action of sodium acetoacetic ester with iodine or with a dihalide such as ethylene bromide:



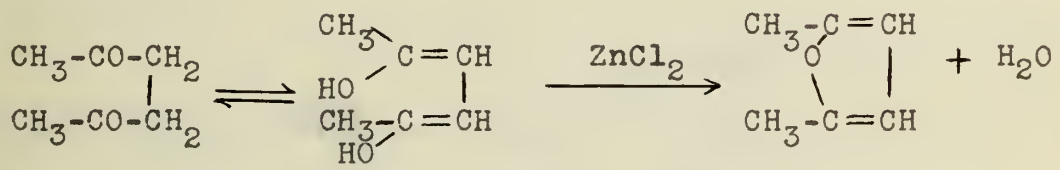
$$\longrightarrow CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}CH_3.$$

Neither of the above methods has been successful in the synthesis of 1-5 diketones, however. Baeyer and Piccard[32] obtained the first saturated aliphatic 1-5 diketone from dimethylpyrone as follows:

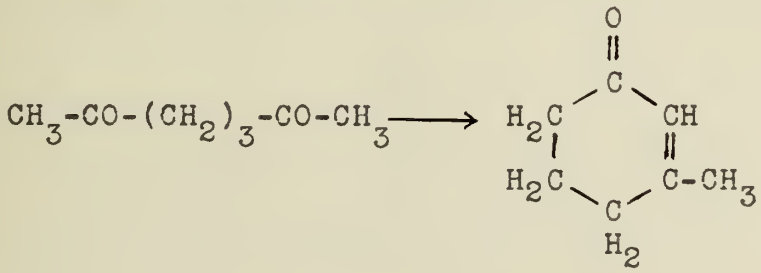


A few years later, Harries[33] obtained diacetyl propane by the action of ozone on caoutchouc, but he did not discover the identity of the product until the following year[34]. Both of these 1-5 diketones were found to split out water very easily, to give a ring structure; minute amounts of alkali caused this change to take place with extraordinary ease.

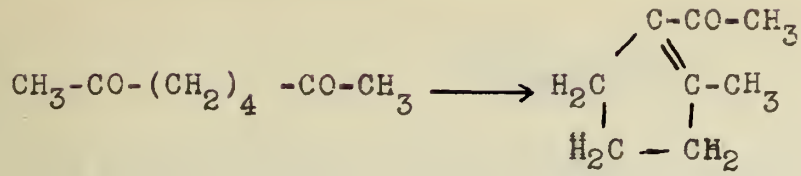
The formation of rings by the elimination of water is characteristic of a number of the diketones. The simplest 1-4 diketone, acetonyl acetone, requires distillation with a dehydrating agent, such as zinc chloride, in order to cause ring formation to take place:



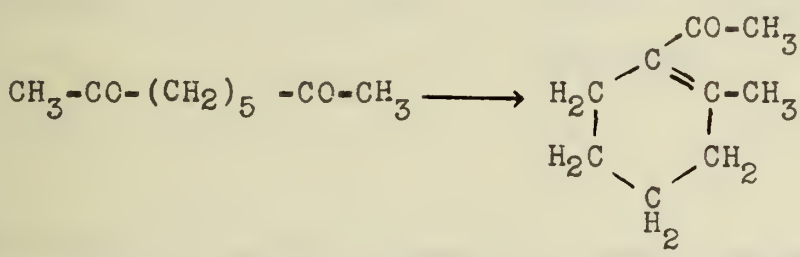
As has been mentioned, the simplest 1-5 diketone, diacetylpropane, rearranges very easily in the presence of even a trace of alkali, or when heated with acids, to give a six-membered ring:



Diacetyl butane, the simplest representative of the 1-6 diketones, rearranges somewhat more slowly than diacetyl propane, and in this case a five-membered ring is obtained:



This change has been found to take place under the influence of dehydrating agents, by boiling with alkali, or merely on distillation. The 1-7 diketones are more stable than the two preceding members of the series; diacetyl pentane does not form a ring with dilute alkali, but does so when boiled with strong sulfuric acid for some time. The ring is a six-membered one, as in the case of 1-5 diketones, and not a five-membered ring as is obtained from the 1-6 diketones:



The 1-8 and 1-9 diketones form no ring structures.

THEORETICAL.

In consideration of the tendency of the 1,5 diketones to split out water and to form a ring in the presence of alkalis, a synthesis of such ketones in neutral or slightly acid solutions should be more promising of success. The reaction of organo-magnesium halides on trimethylene cyanide might therefore be expected to yield the desired diketones, since the solution is neutral until the final decomposition of the Grignard compound with water or acid. The reaction should proceed as follows:

$$N\equiv C(CH_2)_3-C\equiv N + 2\ R\text{-}MgBr \longrightarrow \begin{matrix} R\text{-}C{=}N\text{-}MgBr \\ | \\ (CH_2)_3 \\ | \\ RC{=}N\text{-}MgBr \end{matrix} \xrightarrow{4\ H_2O} R\text{-}CO(CH_2)_3\text{-}COR + 2\ Mg\begin{matrix} Br \\ OH \end{matrix} + 2\ NH_3.$$

According to the above reaction, phenyl magnesium bromide should yield dibenzoyl propane, and ethyl magnesium bromide should give dipropionyl propane. This was not the case, however; the only pure product obtained in the former case was diphenyl, while ethyl bromide gave no better results, the product being a liquid which was too high boiling to permit distillation without decomposition. Benzyl bromide reacted like brombenzene, the product being diphenyl ethane.

The synthesis of 1,5 diketones in this way therefore is not feasible, a mixture of other products being obtained.

EXPERIMENTAL.

The trimethylene cyanide used in the following reactions was prepared according to the method of Henry[35], slightly modified as follows:- To 1500 cc. absolute methyl alcohol in a 2-litre flask, 40 grams potassium cyanide was added and refluxed for a short time. Not all of the potassium cyanide went into solution. 200 grams trimethylene bromide was then added, and the material refluxed on the water bath overnight. The liquid was then cooled and the solid filtered off with suction, 40 grams more potassium cyanide added to the filtrate, and the mixture refluxed as before. This was repeated until 180 grams potassium cyanide had been used up, when the filtrate was distilled over until a thermometer placed in the liquid reached 165°; the remainder of the liquid was distilled under 60 mm. and the fraction 183-6° collected. The yield was 55 grams, or 57% of theory. Henry reported a yield of 80% when the potassium cyanide was all added at once, whereas his method gave only about 40% yield when this method was used by the writer. The difference in yield was doubtless due to the purity of the potassium cyanide used, which was found to have a very appreciable influence on the yield. Henry used pure potassium cyanide, prepared from hydrocyanic acid.

One mole of trimethylene cyanide was dropped on to $2\frac{1}{2}$ moles of ethyl magnesium bromide in dry ether solution, the flask being vigorously shaken during the addition, which required almost an hour. The gray solid, which formed almost immediately when the trimethylene cyanide struck the surface of the liquid, was thus kept in a finely divided condition. The solid turned yellow on

standing, and the material had a pleasant nut odor. After allowing it to stand an hour, water was added until no further reaction took place, and the solution extracted with ether. The ether was evaporated off and the remaining liquid distilled. No definite boiling fractions were obtained, and most of the material charred in the flask.

The reaction of phenyl and benzyl magnesium bromide with trimethylene cyanide was carried out in the same way in the above case; the products obtained were, respectively, diphenyl and diphenylethane. The other products of the reaction were tarry liquids which could not be purified.

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BIOGRAPHY.

The writer was born at Hamilton, Ohio, on August 22, 1893. After the completion of his high school course in 1910, he taught for a year in the public schools of Reilley, Ohio, and the following year entered Miami University. He was assistant in Chemistry in the year 1913-14, and received the degree of Bachelor of Arts in June, 1914. During the summer of 1914 he taught in the Department of Chemistry of Miami University, and in September of the same year took up graduate work in Chemistry in the University of Illinois, where he received the degree of Master of Arts in 1916. During the three years from 1914 to 1917 he was assistant in the Department of Chemistry in the University of Illinois, and was Fellow in the same institution in 1917-18. During the summers of 1915, 1916, and 1917, he was engaged in the manufacture of organic chemicals for the University of Illinois.